AIRBORNE, IN SITU AND LABORATORY MEASUREMENTS OF THE OPTICAL AND PHOTOCHEMICAL PROPERTIES OF SURFACE MARINE WATERS

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LONG TERM GOALS

The principal long-term objectives of this work are 1) to uncover and quantify the primary factors controlling the spatial and temporal distributions of the light-absorbing (colored) constituents of dissolved organic matter (CDOM) in marine and estuarine waters, 2) to determine the impact of CDOM on the aquatic light field and remotely-sensed optical signals, 3) to examine the effects of photooxidation on the optical absorption and emission properties of this material, as well as the relationship between the loss of absorption (and fluorescence) by photooxidation and the yield of photochemical intermediates and products. A combination of field and laboratory measurements are being employed to estimate the wavelength dependence of the rates of the photobleaching response and its relationship to organic carbon photooxidation and the production of photochemical intermediates, in order to better understand the impact of photooxidation on marine carbon and trace element cycles and the optical properties of seawater.

OBJECTIVES

Our near-term objectives have been 1) to complete a series of field studies in 1996 and 1997 devoted to examining the seasonal dependence of CDOM absorption and emission in the Middle Atlantic and its contribution to the aquatic light field, as well as the effects of stratification on the photodegradation of CDOM and on the vertical structure of the optical properties, and 2) to initiate a detailed laboratory study of CDOM photobleaching using both monochromatic and broad band light sources.

APPROACH

One five-day cruise in August 1996 and two seven-day cruises in late May and early August 1997 were performed to examine the optical and photochemical properties of waters in the Middle Atlantic Bight and in the Delaware and Chesapeake Bays. Data obtained from these cruises included: 1) optical absorption spectra of CDOM; 2)

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continuous onboard fluorescence measurements of CDOM; 3) for selected stations, 3-D fluorescence spectra of CDOM; 4) particle absorption spectra using the filter pad method; 5) detrital absorption spectra using the methanol extraction method; 6) DOC concentrations; 7) in-water downwelling irradiance and upwelling radiance using a Biospherical Instruments MER (L. Harding and M. Mallonee); 8) in-water downwelling irradiance in both the UV and visible using a Satlantic SPMR, and above-water irradiance and just below-surface upwelling radiance using the Satlantic surface reference (W. Miller and R. Davis); 9) backscattering coefficients employing a Sequoia Scientific BBC-4 backscatter meter (August 1996); 10) continuous surface chlorophyll fluorescence measurements; 11) pigments, nutrients and primary production at selected stations (L. Harding and M. Mallonee); 12) sampling for laboratory photobleaching and photochemistry experiments. Aircraft overflights of NASA's airborne oceanographic lidar (AOL) were carried out in concert with the two August cruises (F. Hoge). The AOL acquired active measurements of CDOM and chlorophyll fluorescence and passive reflectance measurements.

Samples collected during these cruises were subjected to monochromatic and broad-band irradiation with kinetics of the spectral changes (both absorption and fluorescence) monitored. Other samples were examined to determine the wavelength dependence of the quantum yields for the formation of selected radical species.

WORK COMPLETED

Three (very) large sets of in situ optical and (photo)chemical data, and two major sets of airborne optical data were acquired over the last year. The PI and his collaborators are currently processing and integrating these data. In addition, a preliminary set of photobleaching experiments has been completed and a paper is being prepared for publication.

RESULTS

Although much of the data from the newer field work is still being processed, a preliminary analysis appears to support the conclusion reached in earlier field studies, namely that, in surface waters by late summer, photobleaching can significantly reduce light absorption by CDOM in surface waters and alter the relationship between absorption and DOC concentration due to the photodegradation of CDOM to uncolored DOC and dissolved inorganic carbon. Thus, stratification of the water column during the summer months appears to "trap" CDOM in a shallow mixed layer where it undergoes substantial photobleaching, whereas the CDOM in the deeper waters below the thermocline is protected due to the limited penetration of UV radiation (which is principally responsible for the photobleaching, see below).

This result can be contrasted with that obtained on our recent cruise in late spring (29 May - 4 June 1997). Although stratification of the water-column was evident, the CDOM absorption coefficients of the surface and deep waters fell on the nearly same mixing line.

The absence of a easily discernible photobleaching signal in late (and early) spring is likely due to a number a factors including: 1) mixed-layer depths greater than the UV penetration depth, thus causing the photobleaching signal to be averaged over a greater water-column depth; 2) lower total UV photon dose; 3) the slow kinetics of the photobleaching response (see below).

Further, upon stratification, the phytoplankton population (as determined by fluorescence) largely concentrates as a layer at the base of the thermocline, leading to a situation where CDOM absorption dominates in surface waters whereas phytoplankton absorption dominates in the deeper waters. We would predict that, as the mixed layer shallows during the summer, CDOM absorption will decrease in the surface waters and that the photobleaching signal will become increasingly evident with time. This increased UV transparency of surface waters in late summer may have significant ecological consequences.

Knowledge of the kinetics of the photobleaching response for CDOM is essential for an quantitative analysis of this problem. Thus, over the last year, we initiated a detailed laboratory study of CDOM photobleaching using both broad-band and monochromatic light. The salient results are summarized below:

- Photobleaching exhibits biphasic kinetics with the lifetime of the faster component in the range of 10-30 hr and the lifetime of the slower component in the range of 100-3000 hr, depending on the wavelength of irradiation.

- The rate of absorption (and fluorescence) loss is greatest at the irradiation wavelength, although significant rates of loss are also observed outside the irradiation wavelength. Thus, irradiation with monochromatic light can produce photochemical "hole-burning" in the absorption and in the fluorescence excitation-emission matrix (EEM or 3-D) spectra of the CDOM. The loss of absorption at the irradiation wavelength is likely due to the direct photochemical destruction of the chromophore(s) absorbing at that wavelength, whereas the broad loss of absorption at the other wavelengths may be caused by reactions with secondary photochemical intermediates such as reactive oxygen species.

- The efficiency of both the primary and secondary bleaching decreases with increasing wavelength and is greatest in the UV-B and UV-A.

- The photobleaching kinetics are similar for CDOM from different sources.

These initial results indicate that we will be able to develop a generalized spectral response function from which to predict the environmental rates and spectral dependence of CDOM absorption (and fluorescence) loss.

IMPACT

Because CDOM dominates light absorption in the blue portion of the visible spectrum in surface coastal waters throughout much of the year, it directly impacts underwater visibility and the propagation of visible radiation in the littoral environment. These factors can affect the ability of the operational Navy to detect and identify submerged enemy ordnance and to perform their own operations discreetly in these environs. For these reasons, an understanding of the factors that control the spatial and temporal variability of this material and its impact on the optical properties of coastal waters should be of direct benefit to the Navy.

RELATED PROJECTS

In addition to our continuing collaboration with Dr. Frank Hoge at NASA/Wallops (AOL overflights), we have initiated two additional collaborations over the last year - one with Dr. Larry Harding (University of Maryland) and one with Dr. William Miller and Dr. John Cullen (Dalhousie University). These collaborations have brought additional expertise and field measurement capabilities to bear on the goals of determining the levels of CDOM and photochemical fluxes remotely via airborne and satellite platforms. On our recent cruises in 1996 and 1997, Dr. Larry Harding and his co-workers acquired in-water profiles of downwelling irradiance and upwelling radiance using a Biospherical Instruments Multichannel Environmental Radiometer (MER), in addition to measuring primary productivity (at selected stations) and collecting samples for nutrients and pigments. Dr. Harding also performs regular aircraft overflights of the Chesapeake Bay carrying an ODAS sensor, which measures water leaving radiances at 460, 490 and 520 nm, and more recently a SAS II sensor, which measures downwelling irradiance and water-leaving radiances at the SeaWiFS bands and at five additional bands in the UV, red, and near IR. In the future, we hope to coordinate our field operations as closely as possible to take advantage of these additional measurement capabilities. In addition, Dr. William Miller and Richard Davis (from John Cullen's laboratory) acquired vertical profiles of downwelling irradiance at wavelengths in both the UV and visible using a Satlantic SPMR, as well as concurrent measurements of above-surface downwelling irradiance and just below-surface upwelling radiance using the Satlantic surface reference (SMSR). During the August 1996 cruise, backscattering coefficients were also acquired with a Sequoia Scientific BBC-4 backscatter meter rented from R. Maffione. We hope to maintain these or other comparable collaborations in the future, so that a complete suite of airborne and *in situ* optical measurements will continue to be obtained.